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Correlation analysis of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones

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ABSTRACT

A series of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thione compounds were synthesized and examined their purities as per the literature. The IR spectra of νC=N, νC=S, νNH and νCOC frequencies and NMR chemical shifts (ppm) of δNH, δOCH_3, δCH_2, δC=N, δC=S, δOCH_3 and δCH_2 are also assigned. The assigned IR and both ^1H NMR and ^{13}C NMR spectral data have been correlated with Hammett substituent constants and Swain-Lupton's parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the above spectral data has been studied.

***Keywords*:** 1,2,4-triazole, Hammett constants, Swain-Lupton's parameters, IR spectral, NMR spectral, correlation, multi-regression analysis

1. INTRODUCTION

Triazoles are well known five membered heterocyclic compounds and several procedures were reported for their synthesis. Such studies have been stimulated by various promising applications, especially in the case of nitrogen containing heterocyclic entities. In fact, certain nitrogen containing heterocycles are used as pharmaceutical e.g. analgesic, anti-inflammatory, antipyretic, agrochemicals where as some other is being studied for their medicinal interest.

The knowledge of such applications has point out that nitrogen containing heterocycles are important target to be prepared to our research on medicinally interesting chemical entities. Triazoles have occupied an important place in the drug industry. Hoggarth [1] and Meyer [2] have been studied briefly with the chemistry of 1,2,4-triazoels.

Bladin [3, 4] is a pioneer scientist in the field of triazole, who had synthesized the first derivative of 1,2,4-triazoel in 1885. 1,2,4-triazole derivatives not only known for their medicinal applications, but they are also used as analytical reagents [5], dyes and photographic chemicals [6], corrosion inhibitors [7,8] and in the preparation of polymers [9].

Correlation analysis is useful for prediction of ground state equilibration of organic compounds such as *s-cis* and *s-trans* conformers of unsaturated carbonyl compounds [10], acyl bromides and esters [11].

The *E*- and *Z*- configuration of protons in unsaturated systems [10], spatial arrangement of protons in five membered systems [12, 13]. Qsar and Qpr study was applied for studying the effect of substituents on the spectral frequencies [14].

Recently, Thirunarayanan et. al., [10, 15] have studied the effect of substituents on the spectral frequencies of sydnone based chalcones and oxazoles.

Mayavel et. al. [16] have studied the effect of substituents on some *E*- imines. Within the above view, there is no report available for the study of effect of substituents on the titled compounds.

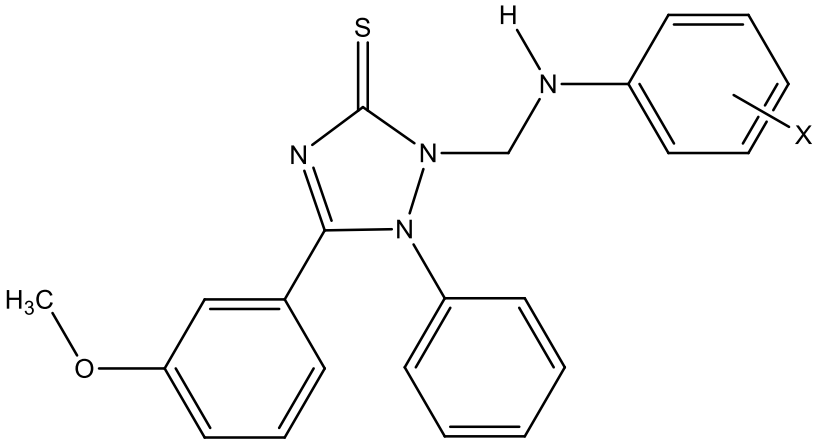
Therefore the authors have taken efforts for the preparation of titled compounds and recorded the IR and NMR spectra for evaluation of effect of substituents on the spectral frequencies.

2. EXPERIMENTAL

In the present study, the series of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thione compounds have been synthesized as shown in literature [17].

The general structure of the above titled compounds is shown in Fig. 1.

The assigned IR group frequencies of νC=N, νC=S, νNH and νCOC and the NMR chemical shift δ(ppm) values of δNH, δOCH_3, δCH_2, δC=N, δC=S, δOCH_3 and δCH_2 of substituted 2-((phenylamino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thione compounds are assigned and are shown in Tables 1 and 2 respectively.



X= H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2

Fig. 1. General structure of substituted 2-((phenylamino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thionederivatives

Table 1. IR spectral data of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thione compounds

Entry	X	νC=N (cm^{-1})	νC=S (cm^{-1})	νNH (cm^{-1})	νC-OCH_3 (cm^{-1})
1	H	1598	1123	3351	1044
2	2-Cl	1592	1124	3326	1042
3	3-Cl	1588	1122	3358	1044
4	4-Cl	1596	1116	3359	1041
5	4-F	1594	1123	3388	1039
6	4-OCH_3	1593	1117	3346	1038
7	2-CH_3	1683	1122	3360	1042
8	3-CH_3	1597	1118	3326	1041
9	4-CH_3	1598	1120	3410	1040
10	2-NO_2	1596	1124	3397	1043
11	3-NO_2	1603	1043	3389	1044
12	4-NO_2	1596	1116	3374	1037

Table 2. The NMR data of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxy phenyl)-1-phenyl-1,2,4-triazole-3-thione compounds.

Entry	X	^{1}H NMR			^{13}C NMR			
		δNH (ppm)	δOCH$_3$ (ppm)	δCH$_2$ (ppm)	δC=N (ppm)	δC=S (ppm)	δOCH$_3$ (ppm)	δCH$_2$ (ppm)
1	H	3.530	3.457	3.749	160.17	187.11	55.63	75.72
2	2-Cl	3.528	3.452	3.741	159.62	187.42	55.74	75.63
3	3-Cl	3.729	3.723	3.885	162.66	187.32	55.81	75.42
4	4-Cl	3.637	3.435	3.828	161.32	187.56	55.93	75.42
5	4-F	3.429	3.568	3.779	161.88	187.63	56.78	75.34
6	4-OCH$_3$	3.669	3.911	3.477	160.48	186.32	55.81	76.07
7	2-CH$_3$	3.308	3.704	4.093	162.38	187.21	58.54	75.31
8	3-CH$_3$	4.109	3.702	4.169	161.31	187.59	58.76	75.18
9	4-CH$_3$	4.112	3.707	4.170	161.52	187.52	58.97	75.19
10	2-NO$_2$	3.562	3.633	3.972	161.22	187.20	58.88	76.32
11	3-NO$_2$	3.569	3.632	3.767	161.89	187.31	58.81	76.39
12	4-NO$_2$	3.571	3.628	3.770	162.02	187.24	59.64	76.41

3. RESULTS AND DISCUSSION

3. 1. Infrared spectral study

The assigned infrared stretching frequency of all 1,2,4-triazole derivatives like $\nu_{C=N}$, $\nu_{C=S,}$ ν_{NH} and ν_{COC} values are presented in Table 1. These spctral data (ν, cm^{-1}) of substituted 2-((phenylamino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thione compounds have been correlated with Hammett substituent constants and F and R parameters. These assigned infrared stretching frequency values are correlated [18-25] with different Hammett substituent constants and *F* and *R* parameters using single and multi-linear regression analyses.

The structure parameter correlation involving group frequencies, the employed Hammett equation is shown in equation (1).

$$\nu = \rho\,\sigma + \nu_0 \qquad \ldots (1)$$

where ν_0 is the frequency of the parent member of this series.

The results of statistical analysis of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thione compounds is shown in Table 3. It is evident that all the substituents except that with parent compound (H), 3-CH_3 and 4-CH_3 substituents have shown satisfactory correlations with Hammett constant σ_I and *F* parameter with respect to IR νC=N (cm^{-1}) frequencies. In case of IR νC=S (cm^{-1}) frequencies, all the compounds except 4-Cl, 3-NO_2 and 4-NO_2 substituents have shown satisfactory correlations with Hammett constant σ^+ only.

The correlations analysis of R νNH (cm^{-1}) frequencies have shown satisfactory correlations with Hammett constants σ, σ^+, σ_I and F parameter. The Hammett constants σ, σ^+, σ_R and R parameter have also shown satisfactory correlations for all.

Table 3. Results of statistical analysis of IR and NMR spectral correlations of substituted 2-((phenyl amino)me*th*yl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thione compounds.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
$\nu_{C=N}$	σ	0.765	1606.59	-18.179	25.71	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.718	1603.69	-8.893	26.28	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.903	1614.50	-34.567	24.63	9	2-Cl,3-Cl,4-Cl,4-F, 4-OCH_3, 2-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.900	1603.10	2.343	26.75	10	H, 2-Cl, 3-Cl, 4-F, 4-OCH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.903	1615.01	-34.222	24.68	9	2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.904	1603.62	4.926	26.72	10	H, 2-Cl, 4-Cl, 4-F, 4-OCH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
$\nu_{C=S}$	σ	0.645	1118.97	-24.062	21.54	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.903	1115.34	-13.889	22.32	9	H, 2-Cl, 3-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2

	σ_I	0.833	1122.83	-26.165	22.30	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.84	1108.86	-43.726	21.63	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.831	1122.70	-24.458	22.48	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.737	1108.44	-34.704	21.97	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
ν_{NH}	σ	0.903	3360.29	24.372	26.38	10	H, 2-Cl , 3-Cl, 4-Cl, 4-OCH_3, 2-CH_3, 3-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.903	3363.71	16.768	26.54	9	H, 3-Cl, 4-Cl, 4-OCH_3, 2-CH_3, 3-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.902	3356.43	26.362	27.03	10	H, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.739	3369.79	37.956	26.92	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.903	3353.39	33.549	26.30	10	H, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.824	3369.63	26.884	27.35	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
ν_{COC}	σ	0.902	1040.99	1.233	2.44	9	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3
	σ^+	0.903	1041.11	1.388	2.36	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.704	1041.38	-0.407	2.49	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2

	σ_R	0.903	1041.71	3.921	2.34	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2
	F	0.741	1041.67	-1.195	2.46	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.904	1041.92	4.207	2.25	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2
δNH	σ	0.726	3.67	-0.151	0.24	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.827	3.66	-0.178	0.23	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.904	3.76	-0.355	0.23	10	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.504	3.65	0.085	0.25	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.904	3.77	-0.352	0.23	10	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.701	3.64	-0.010	0.25	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δOCH_3	σ	0.821	3.64	-0.092	0.13	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.744	3.64	-0.114	0.12	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.724	3.66	-0.099	0.14	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.716	3.61	-0.108	0.14	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3,

							4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.717	3.65	-0.082	0.14	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.725	3.60	-0.157	0.13	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCH_2	σ	0.901	3.87	-0.059	0.21	9	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.718	3.87	-0.051	0.21	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.741	3.98	-0.338	0.18	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.724	3.89	0.277	0.20	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.742	3.98	-0.318	0.19	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.724	3.90	0.222	0.20	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δC=N	σ	0.724	161.25	0.586	0.91	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.716	161.34	0.282	0.93	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.845	161.21	0.462	0.93	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2,3-NO_2, 4-NO_2

	σ_R	0.845	161.45	0.685	0.93	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.871	161.15	0.625	0.92	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.812	161.44	0.467	0.94	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δC=S	σ	0.901	187.25	0.154	0.36	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.902	187.27	0.155	0.35	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2,4-NO_2
	σ_I	0.726	187.27	0.039	0.36	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.725	187.30	0.202	0.36	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.702	187.24	0.104	0.36	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.901	187.32	0.230	0.36	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δOCH_3	σ	0.81	57.18	1.418	1.61	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.721	57.42	0.531	1.68	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.701	57.50	-0.094	1.71	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2

	σ_R	0.906	58.03	4.779	1.35	10	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.702	57.42	0.160	1.71	12	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 2-CH_3 ,3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.905	58.03	3.489	1.46	10	2-Cl, 3-Cl, 4-Cl, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCH_2	σ	0.907	75.51	0.873	0.34	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.906	75.64	0.530	0.39	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-CH_3, 3-CH_3,4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.905	75.84	1.247	0.41	10	H, 2-Cl, 3-Cl, 4-Cl, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.905	75.84	1.247	0.41	10	H, 2-Cl, 3-Cl, 4-Cl, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.905	75.35	0.962	0.40	11	H, 2-Cl, 3-Cl, 4-Cl, 4-OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.905	75.86	1.015	0.42	10	H, 2-Cl, 3-Cl, 4-Cl, 2-CH_3, 3-CH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
r = correlation coefficients; I = intercept; ρ = slope; s = standard deviation; n = number of correlated derivatives							

The compounds except 3-NO_2 and 4-NO_2 substituents with respect to single-linear analysis of IR νC-OCH_3 (cm^{-1}) frequencies of all the 1,2,4-triazoles synthesised. Some of the Hammett constants and F and R parameters have shown poor correlations.

This is attributed with weak polar, inductive, field and resonance effect of the substituents to predict their electronic effects through resonance as per the conjugative structure shown in Fig. 2.

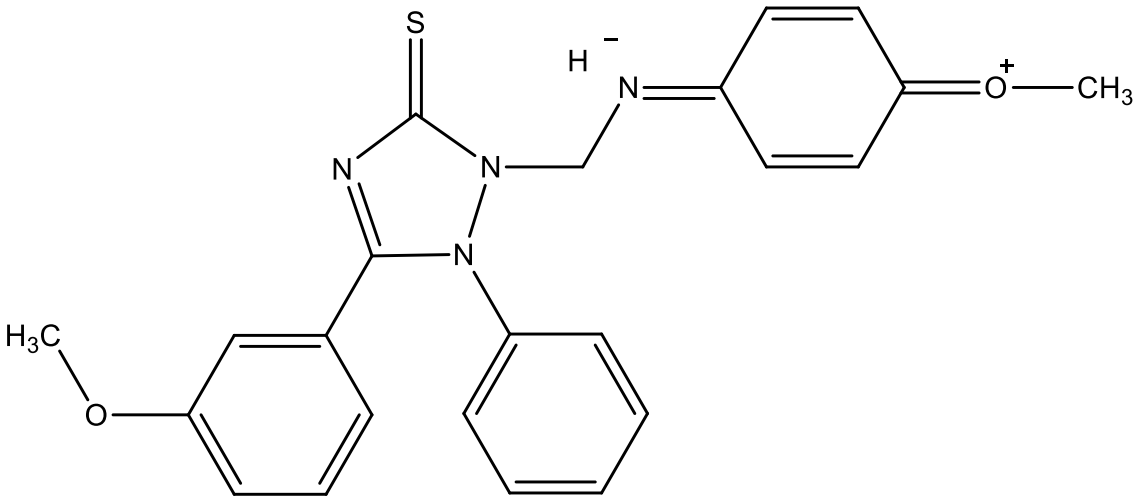


Fig. 2. Resonance conjugative structure.

Most of the correlations have shown positive ρ values and it indicates that operation of normal substituents with respect to IR frequencies. Some of the single-linear plots are shown in Fig. (3-5).

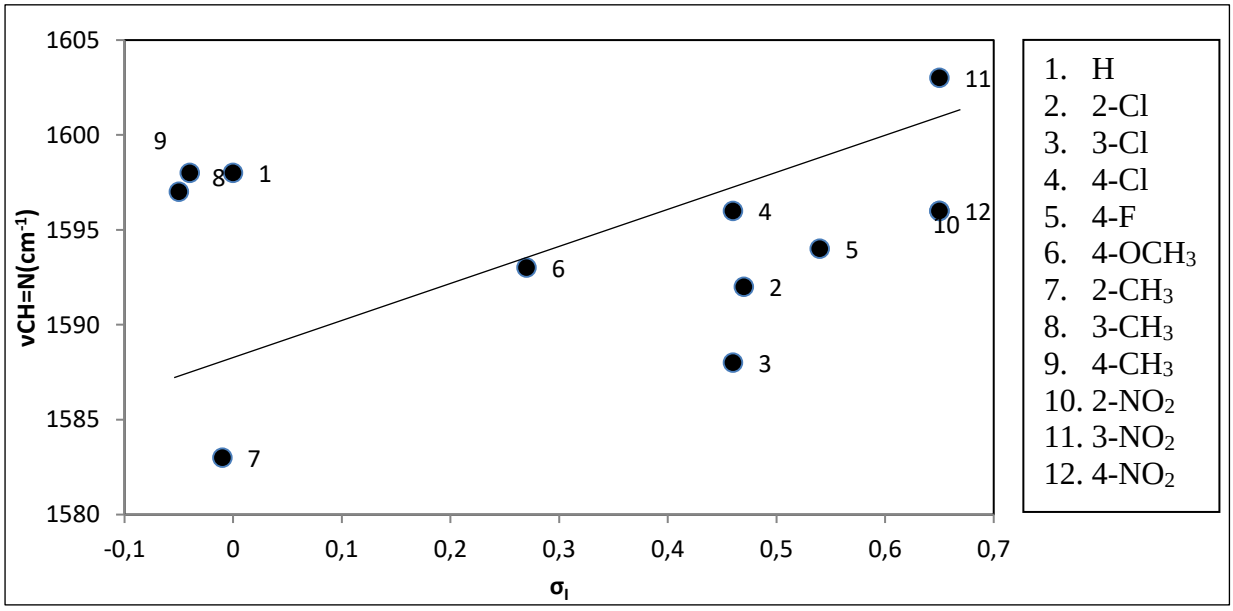


Fig. 3. Plot of νCH=N (cm^{-1}) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ_I

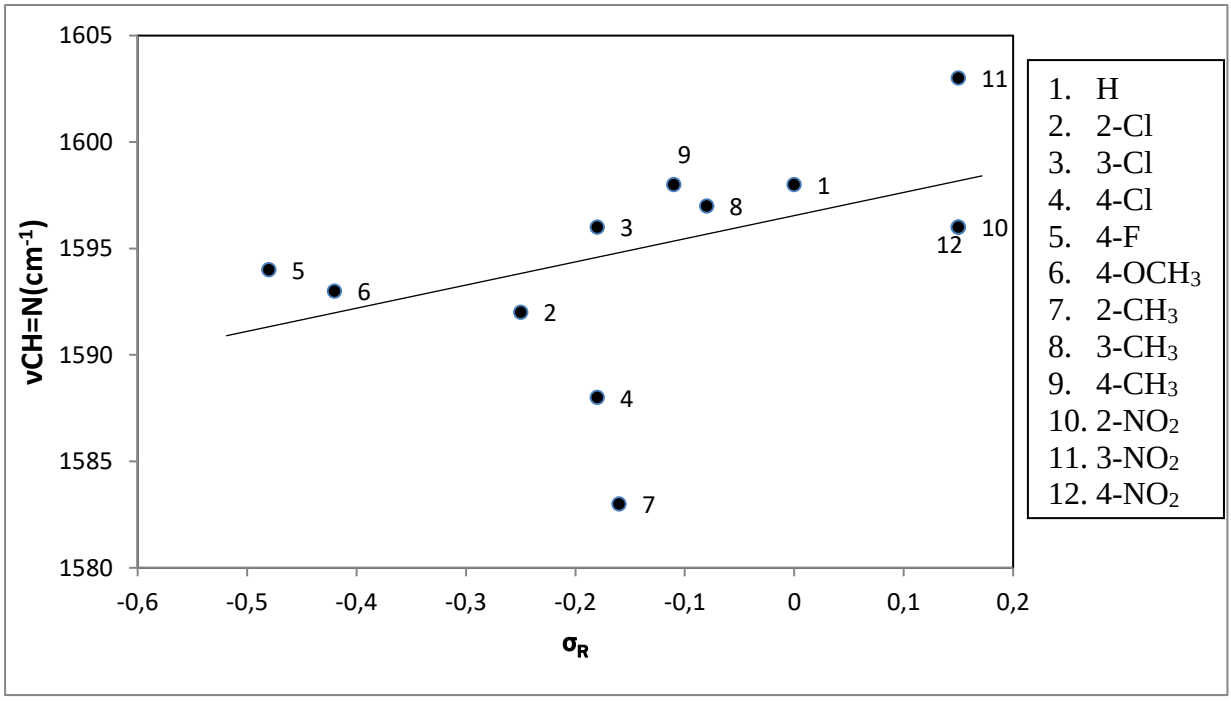


Fig. 4. Plot of νCH=N (cm^{-1}) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ_R.

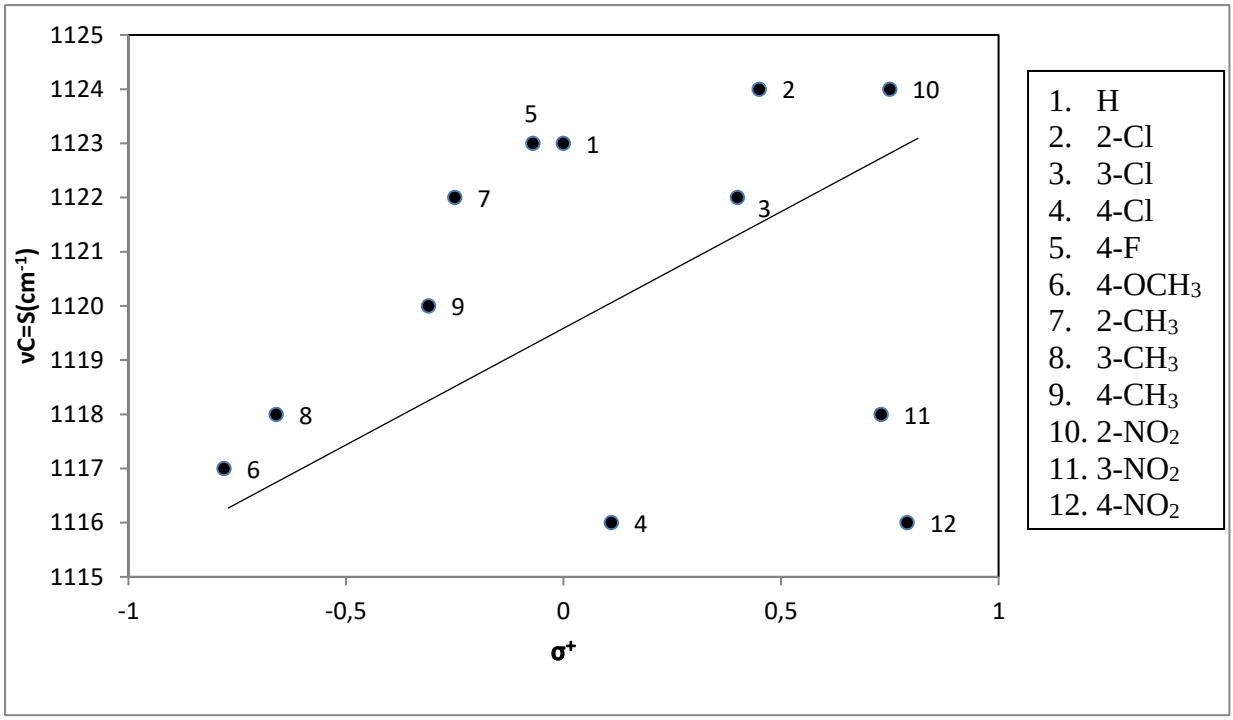


Fig. 5. Plot of νC=S (cm^{-1}) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ^+

The single parameter correlations with Hammett constants and F and R parameters were not obeyed in the regression. While seeking these parameters in multi-regression, inductive and resonance and Swain-Lupton's [26] parameters, they gave satisfactory correlations with the infrared group frequencies. The multi correlation equations are given in (2 – 9).

$$\nu_{C=N}\,(cm^{-1}) = 1616.385(\pm13.304) - 36.122(\pm4.505)\sigma_I + 11.575(\pm2.942)\sigma_R \quad \ldots (2)$$
(R = 0.943, n = 12, P > 90%)

$$\nu_{C=N}\,(cm^{-1}) = 1616.632(\pm 13.658) - 34.878(\pm 4.293)F + 8.673(\pm 1.548)R \quad \ldots (3)$$
(R = 0.939, n = 12, P > 90%)

$$\nu_{C=S}\,(cm^{-1}) = 1116.585(\pm11.247) - 21.013(\pm2.253)\sigma_I - 38.356(\pm4.077)\sigma_R \quad \ldots (4)$$
(R = 0.948, n = 12, P > 90%)

$$\nu_{C=S}\,(cm^{-1}) = 1116.66(\pm 11.641) - 22.051(\pm 2.263)F - 32.339(\pm 3.741)R \quad \ldots (5)$$
(R = 0.946, n = 12, P > 90%)

$$\nu_{NH}\,(cm^{-1}) = 3361.7(\pm14.180) + 22.020(\pm 2.317)F + 32.328(\pm 3.441)R \quad \ldots (6)$$
(R = 0.937, n = 12, P > 90%)

$$\nu_{NH}\,(cm^{-1}) = 3357.781(\pm14.236) + 31.776(\pm2.449)\sigma_I + 23.470(\pm2.926)\sigma_R \quad \ldots (7)$$
(R = 0.947, n = 12, P > 90%)

$$\nu_{COC}\,(cm^{-1}) = 1042.066(\pm1.261) - 0.967(\pm 0.060)F + 4.168(\pm 1.599)R \quad \ldots (8)$$
(R = 0.936, n = 12, P > 90%)

$$\nu COC\,(cm^{-1}) = 1042.492(\pm1.227) - 1.526(\pm0.452)\sigma_I + 4.371(\pm0.924)\sigma_R \quad \ldots (9)$$
(R = 0.946, n = 12, P > 90%)

3. 3. NMR Spectral correlation analysis

3. 3. 1. ^{1}H NMR spectral correlation analysis

The assigned chemical shifts values are presented in Table 2. In nuclear magnetic resonance spectra, the proton or the ^{13}C chemical shifts (δ) depends on the electronic environment of the nuclei concerned. The assigned chemical shifts (ppm) have been correlated with reactivity parameters using the following Hammett equation (10),

$$\delta = \delta_0 + \rho\sigma \quad \ldots (10)$$

where δ_0 is the chemical shift of unsubstituted system.

From the ^{1}H NMR spectra of 1,2,4-triazole derivatives the chemical shifts (δ, ppm) NH, OCH_3 and CH_2 are assigned and tabulated in Table 2. These chemical shifts were correlated with Hammett substituent constants, F and R parameters. The statistical analysis [18-25] of these chemical shifts is presented in Table 3. From Table 3, the NH chemical shifts (δ, ppm) of all the synthesised 1,2,4-triazole derivatives except 3-CH_3 and 4-CH_3 substituents have shown satisfactory correlation with Hammett constant σ_I and F parameter.

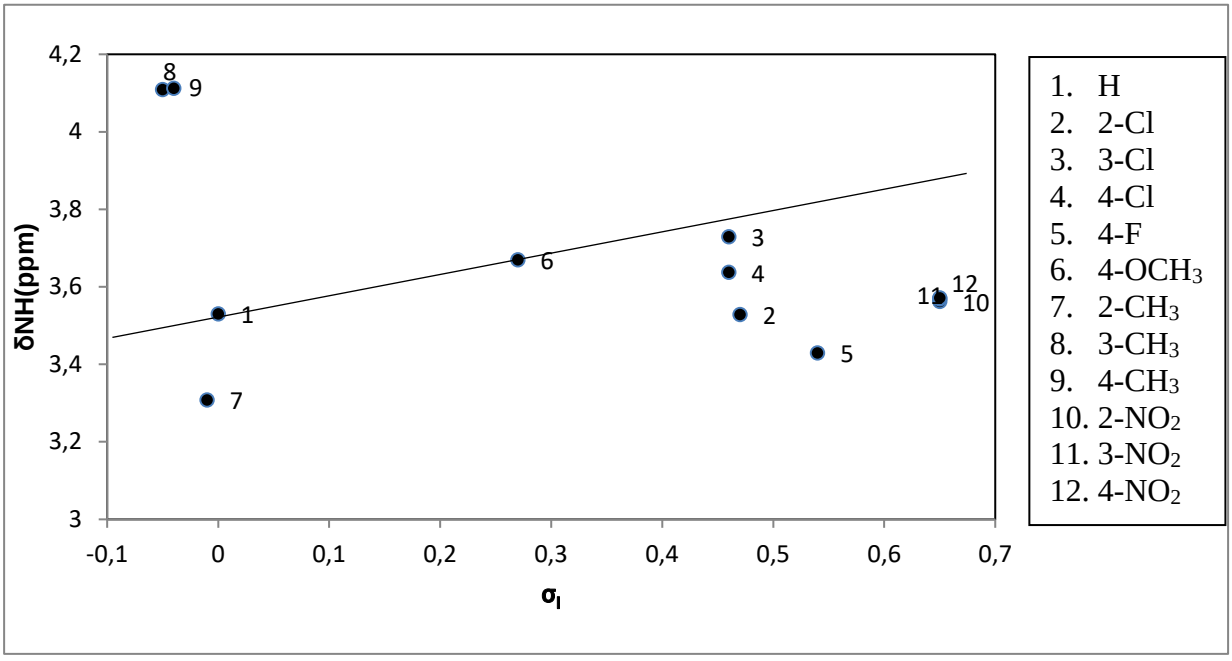


Fig. 6. Plot of ^{1}H NMR δNH (ppm) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ_I

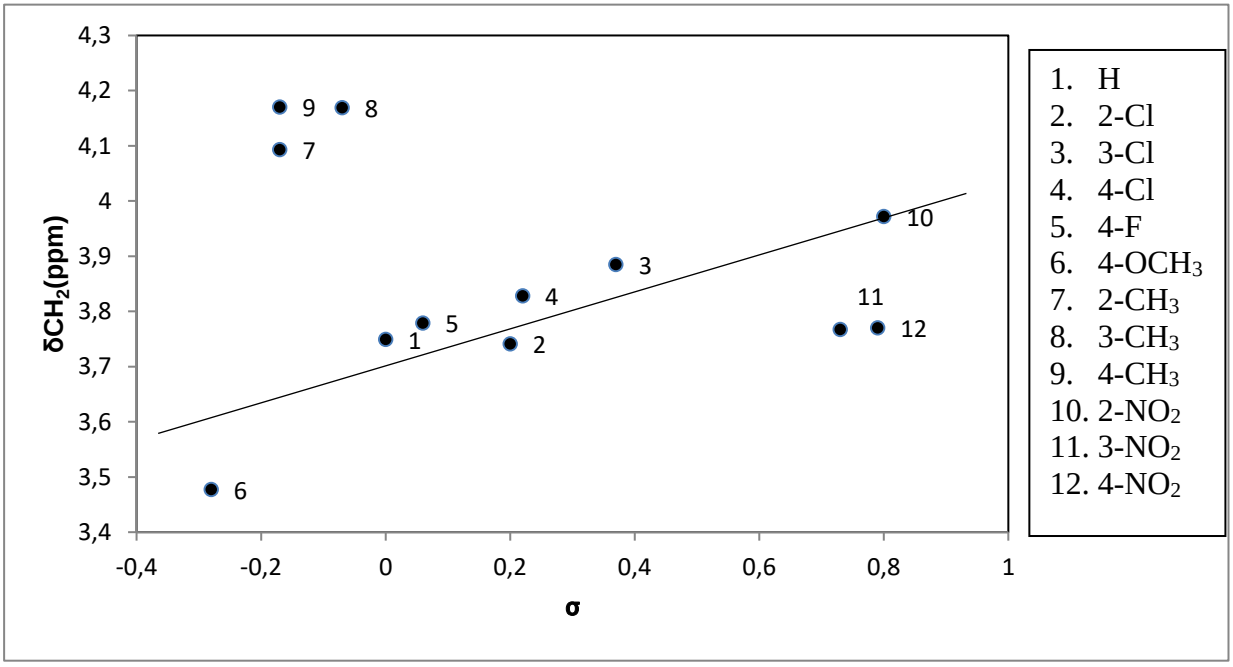


Fig. 7. Plot of ^{1}H NMR δCH_2 ppm) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ

In case of chemical shifts of methylene protons δCH_2 (ppm) have shown satisfactory correlation with Hammett constant σ only. However, the δOCH_3 (ppm) chemical shifts of all the compounds have shown poor correlations with all the Hammett substituent constants and F and R parameters.

This is attributed with weak polar, inductive, field and resonance effect of the substituents to predict their electronic effects through resonance as per the conjugative structure shown in Fig. 2. Most of the correlations have shown positive ρ values and it indicates that operation of normal substituents with respect to ^{1}H NMR chemical shift values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones. Some of the single-linear plots are shown in Fig. (6 and 7).

Some of the single regression analyses have shown poor correlations with Hammett substituent constants and Swain-Lupton's parameters [26]. It is decided to go for multi-regression, the multi-regression analysis produced satisfactory correlations with the chemical shifts of (δ, ppm) NH, OCH_3 and CH_2. The multi correlation equations are given in **(11-16)**.

$$\delta NH \text{ (ppm)} = 3.795(\pm 0.123) - 0.379(\pm 0.025)\sigma_I + 0.182(\pm 0.035)\sigma_R \quad \ldots (11)$$
$$(R = 0.944, n = 12, P > 95\%)$$

$$\delta NH \text{ (ppm)} = 3.776(\pm 0.128) - 0.354(\pm 0.025)F + 0.027(\pm 0.003)R \quad \ldots (12)$$
$$(R = 0.941, n = 12, P > 95\%)$$

$$\delta OCH_3 \text{ (ppm)} = 3.648(\pm 0.075) - 0.088(\pm 0.001)\sigma_I - 0.085(\pm 0.002)\sigma_R \quad \ldots (13)$$
$$(R = 0.924, n = 12, P > 95\%)$$

$$\delta OCH_3 \text{ (ppm)} = 3.630(\pm 11.641) - 22.051(\pm 2.263)F - 32.339(\pm 3.741)R \quad \ldots (14)$$
$$(R = 0.931, n = 12, P > 95\%)$$

$$\delta CH_2 \text{ (ppm)} = 4.402(\pm 0.091) - 0.389(\pm 0.189)F + 0.377(\pm 0.261)R \quad \ldots (15)$$
$$(R = 0.961, n = 12, P > 95\%)$$

$$\delta CH_2 \text{ (ppm)} = 4.028(\pm 0.099) - 0.338(\pm 0.198)\sigma_I + 0.258(\pm 0.937)\sigma_R \quad \ldots (16)$$
$$(R = 0.954, n = 12, P > 95\%)$$

3. 3. 2. ^{13}C NMR spectral correlation analysis

The chemical shifts of C=N, C=S, OCH_3 and CH_2 (δ, ppm) carbons of 1,2,4-triazole derivatives were assigned and tabulated in Table 2. These chemical shifts are correlated [18-25] with Hammett substituent constants, F and R parameters. The results of statistical analysis are shown in Table 3. From Table 3, all the compounds except 4-OCH_3 substituent have shown satisfactory correlations with Hammett constants σ, σ^+ and R parameter. In case of δ OCH_3 (ppm) chemical shifts, all the compounds except parent compound H and 4-F substituent have shown satisfactory correlations with R parameter only.

In case of chemical shifts of methylene carbons δCH_2(ppm) have shown satisfactory correlations with Hammett constants σ and σ^+ for all the compounds except 4-OCH_3 substituent. All the compounds except 4-F and 4-OCH_3 substituents have shown satisfactory correlations with Hammett constants σ_I, σ_R and R parameter. The F parameter has also shown satisfactory correlation with all the compounds except 4-F substituent.

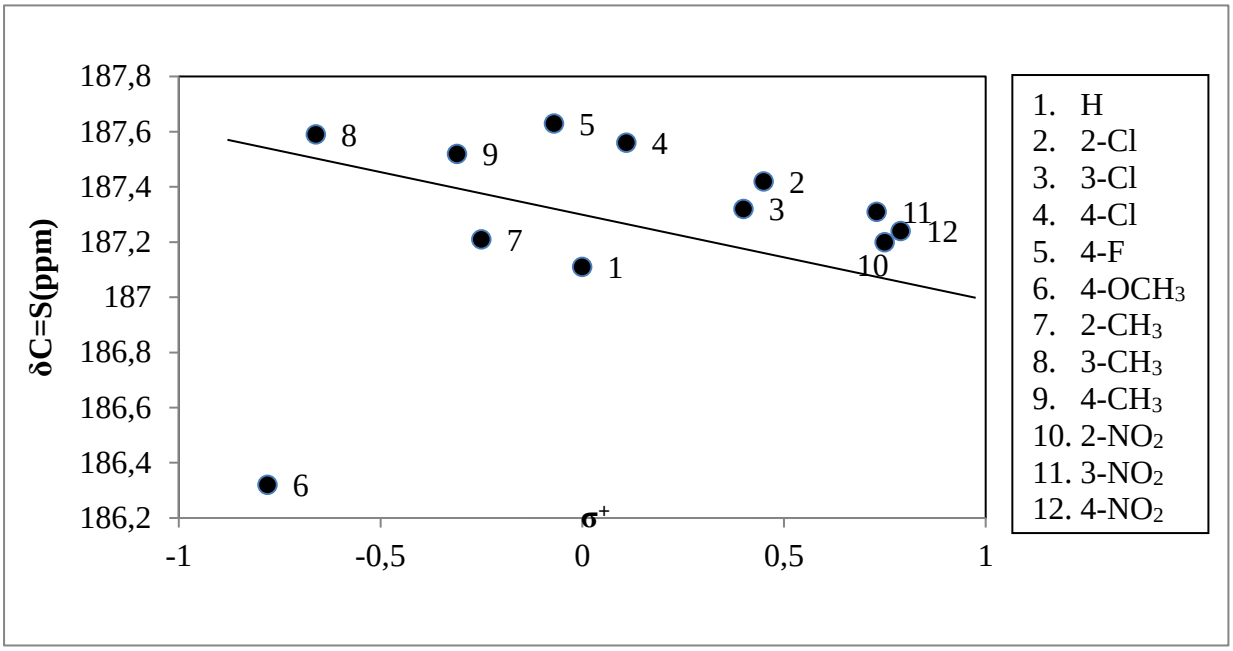


Fig. 8. Plot of ^{13}C NMR δC=S (ppm) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ^+

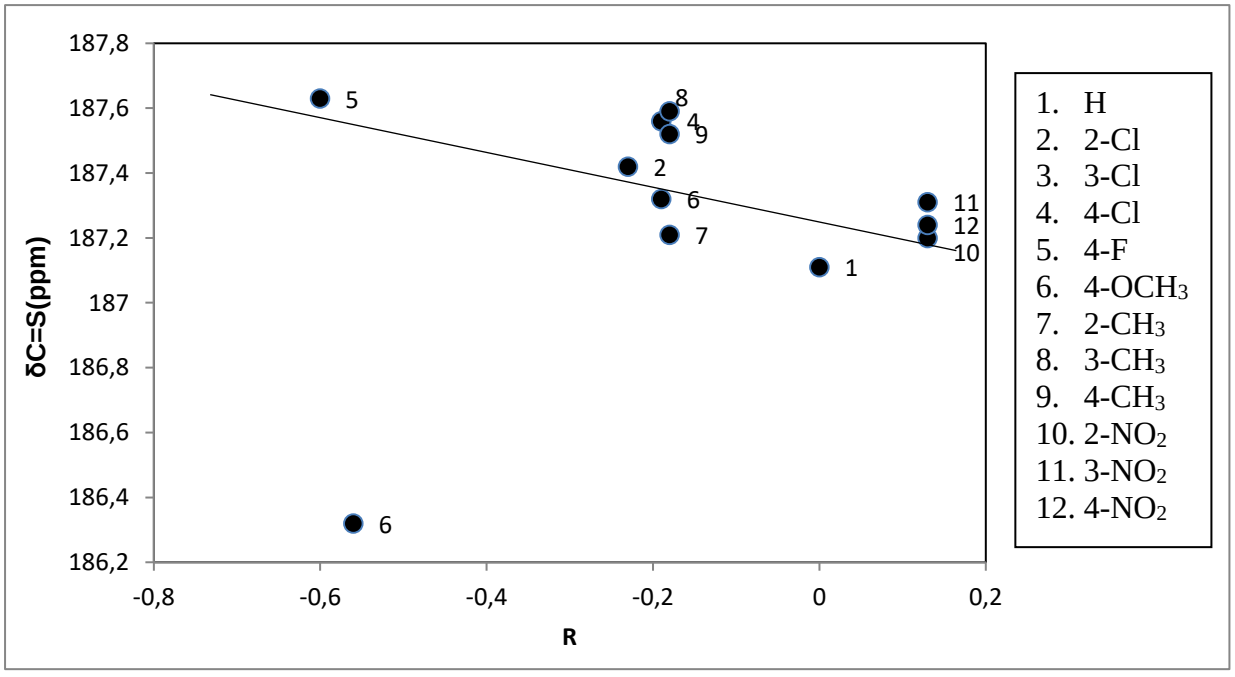


Fig. 9. Plot of ^{13}C NMR δC=S (ppm) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs R.

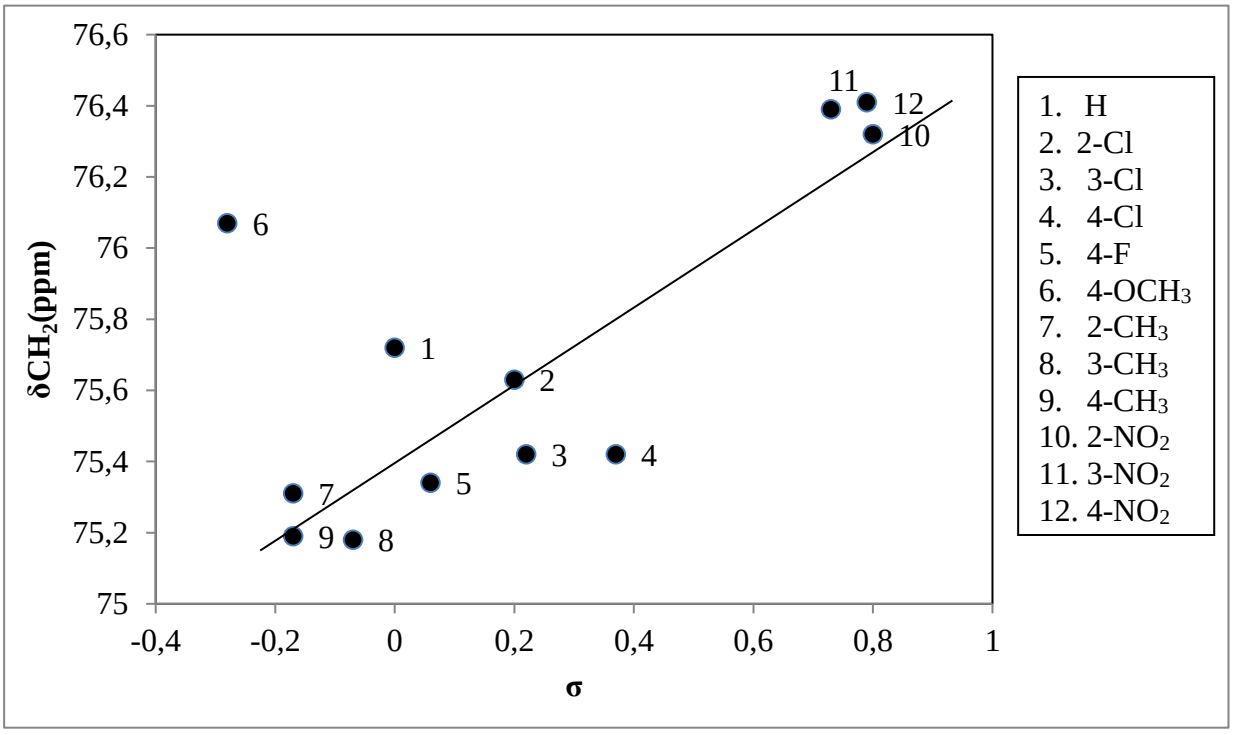


Fig. 10. Plot of ^{13}C NMR δCH_2 (ppm) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ

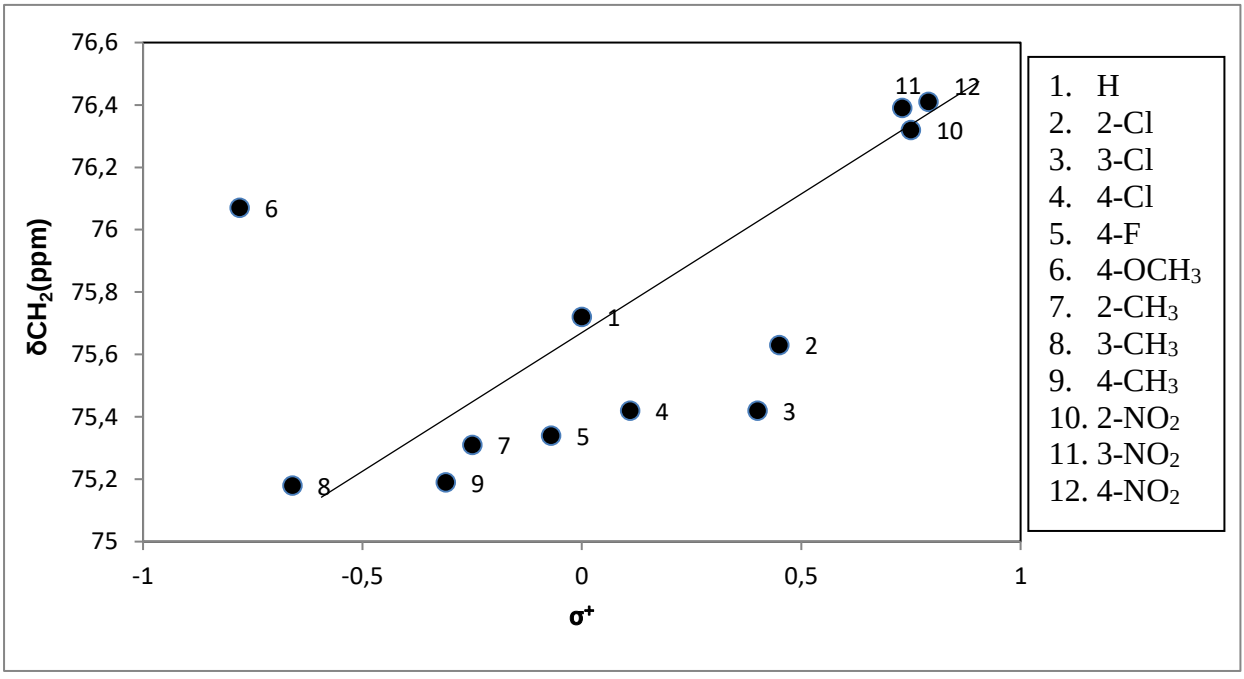


Fig. 11. Plot of ^{13}C NMR δCH_2(ppm) values of substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones Vs σ^+

These substituents that have been given exception in each case are included in regression they reduce the correlations considerably. All the correlations with Hammett constants and F and R parameters are found to fail with chemical shifts of δCH_2(ppm) of 1,2,4-triazole derivatives. This is attributed with weak polar, inductive, field and resonance effect of the substituents to predict their electronic effects through resonance as per the conjugative structure shown in Fig. 2.

Most of the correlations have shown negative ρ values and some of them shown positive ρ values. Negative ρ value indicates the operation of reverse substituent effect and positive ρ value responds operation of normal substituent effect with respect to their spectral data. Some of the single-linear plots are shown in Fig. (8 and 11).

The multi regression analysis of carbonyl carbon, C=N, C=S, OCH_3 and CH_2 chemical shifts (δ, ppm) of 1,2,4-triazole derivatives were satisfactorily correlated with σ_I, σ_R and Swain-Luptons'[26] F and R parameters. The multi-regression equations (17-23) are given below.

$$\delta C{=}N\ (ppm) = 161.31(\pm 0.504) + 0.384(\pm 0.042)\sigma_I + 0.581(\pm 0.043)\sigma \quad \ldots (17)$$
$$(R = 0.919,\ n = 12,\ P > 95\%)$$

$$\delta C{=}N\ (ppm) = 161.22(\pm 0.512) + 0.594(\pm 0.024)F + 0.403(\pm 0.022)R \quad \ldots (18)$$
$$(R = 0.922,\ n = 12,\ P > 95\%)$$

$$\delta C{=}S\ (ppm) = 187.30(\pm 0.197) + 0.012(\pm 0.0407)\sigma_I + 0.199(\pm 0.056)\sigma_R \quad \ldots (19)$$
$$(R = 0.912,\ n = 12,\ P > 95\%)$$

$$\delta C{=}S\ (ppm) = 187.28(\pm 0.200) + 0.087(\pm 0.039)F + 0.221(\pm 0.047)R \quad \ldots (20)$$
$$(R = 0.917,\ n = 12,\ P > 95\%)$$

$$\delta OCH_3\ (ppm) = 58.\ 319(\pm 0.726) - 0.762(\pm 0.502)F + 4.973(\pm 0.207)R \quad \ldots (21)$$
$$(R = 0.962,\ n = 12,\ P > 95\%)$$

$$\delta OCH_3\ (ppm) = 58.\ 074(\pm 0.816) - 0.103(\pm 0.631)F + 3.500(\pm 0.945)R \quad \ldots (22)$$
$$(R = 0.951,\ n = 12,\ P > 95\%)$$

$$\delta CH_2\ (ppm) = 75.502(\pm 0.167) + 0.935(\pm 0.347)\sigma_I + 1.008(\pm 0.478)\sigma_R \quad \ldots (\mathbf{23})$$
$$(R = 0.978,\ n = 12,\ P > 95\%)$$

4. CONCLUSIONS

The IR and NMR spectral data of all the substituted 2-((phenyl amino)methyl)-1,2-dihydro-5-(3-methoxyphenyl)-1-phenyl-1,2,4-triazole-3-thiones have been correlated with Hammett sigma constants and *F* and *R* parameters using single and multi-linear regression analysis. The single parameter correlation with few Hammett constants and Swain-Lupton's parameters gave satisfactory correlation coefficients whereas all multiple correlations gave satisfactory correlation coefficients with Inductive, Resonance, Field and Swain-Lupton's parameters.

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